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Research paper

Organic matter accumulation, redox, and diagenetic history of the Marcellus Formation, southwestern Pennsylvania, Appalachian basin

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ABSTRACT

Variations in the concentration of redox sensitive elements combined with pyrite framboid size data documented from a Marcellus Formation (Middle Devonian) core recovered from southwestern Pennsylvania elucidate the redox, organic matter accumulation, and diagenetic history of these deposits in this region of the basin. Uranium and Mo enrichment and Fe/Al display sharp increases coincident with diminishing Th/U upward through the initial 3rd order trangressive systems tract (lower Union Springs Member). These data as well as abundant small (<6 μm) pyrite framboids record establishment of strongly reducing benthic conditions, perhaps related to the expansion of an oxygen minimum zone induced by increased surface productivity. Strongly anoxic, even euxinic, conditions were interrupted by episodes of dysoxia, perhaps seasonal or longer term. Overlying regressive systems tract (RST) deposits record modestly improved redox conditions, likely a reflection of a receding oxygen minimum zone as base level dropped. A subsequent 3rd order base level rise and renewed expansion of the oxygen minimum zone triggered by increased surface productivity resulted in the accumulation of the organic-rich lower Oatka Creek Member. Still, the mix of abundant small and subordinate large (>10 μm) framboids preserves the record of oxygen deficient to sulfidic bottom conditions frequently interrupted by episodes of (dys)oxia. Improving redox conditions through the overlying RST were accompanied by a two-fold increase in Al and consequent dilution of the organic matter flux and authigenic trace metal uptake at the sediment–water interface. The upper half of the Oatka Creek comprises a depositional sequence not obvious from core inspection or gamma-ray signature but revealed by Mo enrichment and Al concentration profiles. Diagenetic modification of the Marcellus includes several horizons of authigenic calcium carbonate concretions and marked Ba enrichment. Both features reflect the effects of non-steady state microbial diagenesis within a methane-rich sedimentary column.

1. Introduction

The abundance of organic carbon preserved in modern and ancient sedimentary deposits reflects the interplay of various oceanographic and sedimentological factors, including primary surface productivity, bottom-water oxygen supply, nutrient availability, the flux of clastic sediment, and the activity of such degradation processes as bacterial sulfate reduction (e.g. Demaison and Moore, 1980; Calvert, 1987; Tyson, 1995, 2005; Pedersen and Calvert, 1990; Wignall, 1994; Caplan and Bustin, 1998). Until the 1990s, views concerning the origin of ancient marine black shale deposits generally gravitated to one of two schools of thought. The "preservation" paradigm (e.g., Demaison and Moore, 1980) held that the formation of organic-rich sedimentary facies was controlled principally by water column stratification enhanced by the isolation of nutrient-rich anoxic bottom water from the photic zone by a density barrier. The "productivity" school of thought (e.g., Pedersen and Calvert, 1990; Calvert et al., 1992) related the establishment of bottom water anoxia to enhanced surface water productivity. The resulting increased rate of organic matter delivery to the ocean floor drove benthic oxygen demand beyond its rate of resupply by water column mixing establishing anoxic bottom water conditions (Müller and Suess, 1979; Huc, 1988). Variations in the amount of fine-grained clastic sediment delivered to the basin was shown to influence the concentration of organic matter either by accelerating the rate of passage of organic matter through geochemical zones of intense organic degradation or by diluting the organic matter flux (Ibach, 1982; Sageman et al., 2003). It is

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likely that no single factor accounts for organic matter accumulation and preservation in all black shale deposits (Arthur and Sageman, 1994; Canfield, 1994; Rimmer et al., 2004).

This paper examines the organic matter accumulation, redox, and diagenetic history of the Middle Devonian Marcellus Formation preserved in a core recovered from the southwestern Pennsylvania region of the Appalachian basin (Fig. 1) by use of several well-described redox proxies, including Mo and U concentration and Th/U and Fe/Al elemental ratios. The use of paleo-redox proxies is critical to the assessment of hydrocarbon source rock potential given the significant role of water-column and interstitial water chemistry to the preservation of organic matter. Results of the geochemical proxy analysis are complimented by consideration of the size distribution of pyrite framboids, an especially useful indicator of water-column oxygen conditions of modern and ancient sediments. Specific goals of this investigation include:

i) consideration of the roles of productivity and preservation in the accumulation of the organic-rich Marcellus Formation;
ii) assessment of the influence of clastic sediment flux on organic matter concentration in the Marcellus Formation;
iii) generation of a high-resolution redox history of the Marcellus Formation;
iv) recognition of the very early diagenetic history of what appears to have been a methane-rich succession;
v) consideration of the above in terms of the sequence stratigraphy of the Marcellus Formation.

Sedimentary facies analysis of carbonaceous and pyritiferous sediment and sedimentary rock employs a range of terms used to describe the oxygenation levels of bottom and pore water. Here we adopt the nomenclature advanced by Tyson and Pearson (1991), including their definition of bottom water as that part of the water column within a meter of the sediment–water interface. Specifically, we employ the following redox terms and their corresponding oxygen levels; oxic (>2.0 ml O_2 L^{-1}), dysoxic (~0.2–2.0 ml O_2 L^{-1}), suboxic (0.2–0 ml O_2 L^{-1}), and anoxic (0 ml O_2 L^{-1}, 0 ml H_2S L^{-1}). Euxinic or anoxic–sulfidic water lacks O_2 and contains free H_2S (Raiswell and Berner, 1985).

2. Geologic setting

The Middle Devonian Marcellus Formation, the basal unit of the Hamilton Group, accumulated as part of the Catskill Delta complex, an eastward-thickening wedge of clastic marine and terrestrial deposits shed to the west and southwest (present

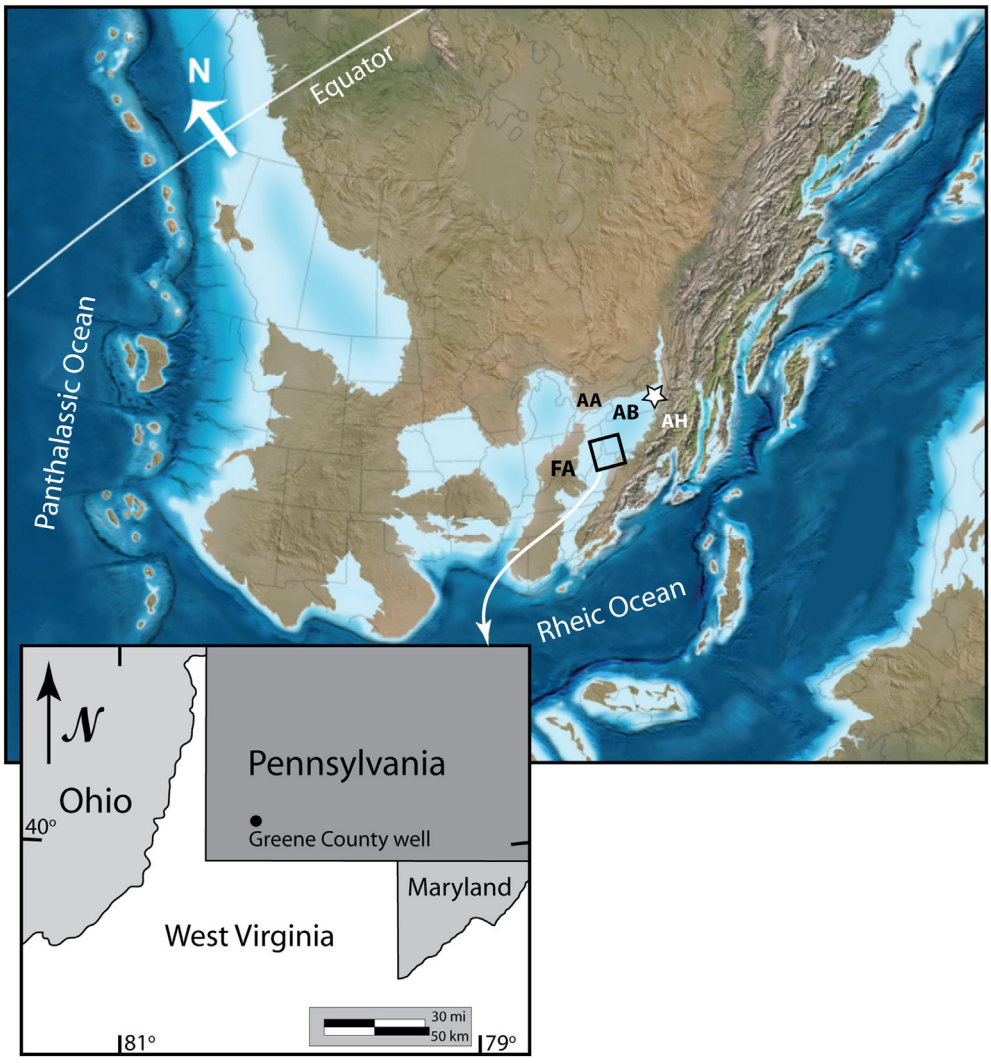

Figure 1. Inferred Middle Devonian paleogeography of Laurentia (modified after Blakey, 2013). Inset shows the location of the Greene County core in southwestern Pennsylvania. Geographic abbreviations: AA = Algonquin Arch; AB = Appalachian Basin; FA = Findlay Arch; AH = Acadian highlands. The star denotes the location of the Beaver Meadows core discussed in the text.